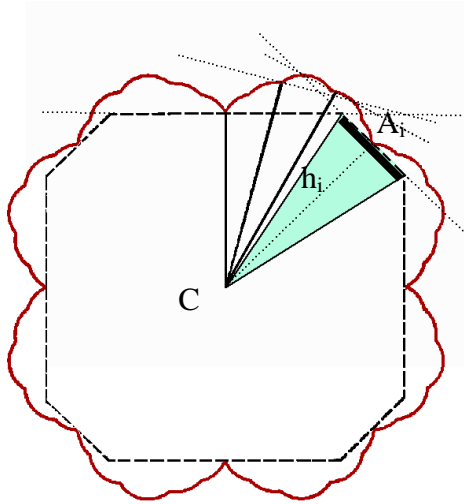


## Lesson 02 Thermodynamics-II

### Equilibrium shape of crystals: Wulf's theorem



Unlike in the liquid materials we have been studying till now, the surface tension of crystalline solid materials depends on the atomic arrangement at the surface, which depends on the orientation, i.e., on the surface Miller indices (to be described later). For that reason the equilibrium shape of a crystal as it solidifies from a liquid drop or condenses from its vapor, changes from spherical to polyhedral. Intuitively one expects surface orientations with low surface tension to be predominant. This will undoubtedly include the most compact surfaces, i.e., those with low

Miller indices, since there the number of broken bonds per atom is minimal. The first treatment of the problem was by Wulf in 1901. Here is his theorem:

Consider a crystal polyhedron (broken lines in the figure) delimited by surfaces of area  $A_i$ , in equilibrium with its vapor. These surfaces are at a distance  $h_i$  from the center C. Large surfaces are closer to the center than smaller ones, as shown in the figure.

In equilibrium we must have:  $\delta\Omega = -p_s\delta V_s - p_v\delta V_v + \sum_i \gamma_i \delta A_i = 0$

The conditions are:

- total volume constant  $V = V_s + V_v$
- same chemical potential  $\mu_s = \mu_v$
- uniform temperature  $T = \text{constant}$

The crystal volume is:  $V_s = \sum_i \frac{1}{3} A_i h_i$ , so that  $\delta V_s = \frac{1}{3} \sum_i [h_i \delta A_i + A_i \delta h_i]$

From the figure we see also that:  $\delta V_{s,i} = A_i \delta h_i = \frac{1}{3} (h_i \delta A_i + A_i \delta h_i) = \frac{1}{2} (h_i \delta A_i)$ .

Substituting into  $\delta\Omega$ , with  $\delta V_s = -\delta V_v$ , we get:

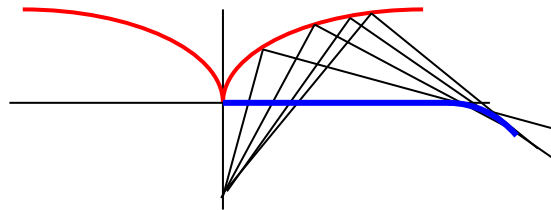
$$\sum_i \left\{ \frac{1}{2} (-p_s + p_v) h_i + \gamma_i \right\} \delta A_i = 0$$

This should be true for any value of  $\delta A_i$  (they are independent variables). Therefore,

$$\gamma_i / h_i = \text{constant}$$

This is Wulff's theorem. It implies that the areas of the facets exposed by the crystal can be obtained by tracing radii in the appropriate direction with a length proportional to  $\gamma_i$  and a plane perpendicular to the radius vector. The minimal polyhedron delimited by the intersection of the innermost planes is the equilibrium shape.

Although the construction in the previous figure shows flat surfaces delimiting the crystal polyhedron, it is not obvious that the flat facet under a sharp cusp (a low Miller index plane) should be delimited by other flat facets, as indicated in the drawing. In fact the envelope of tangents can be curved.

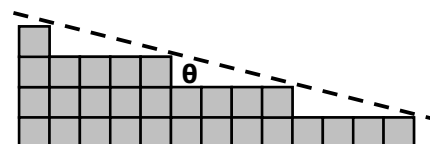
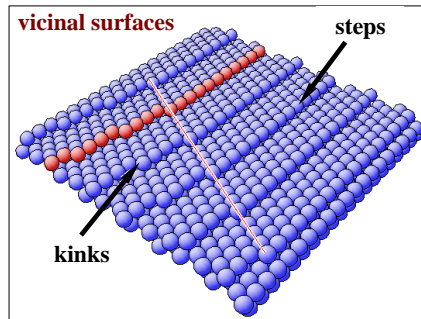
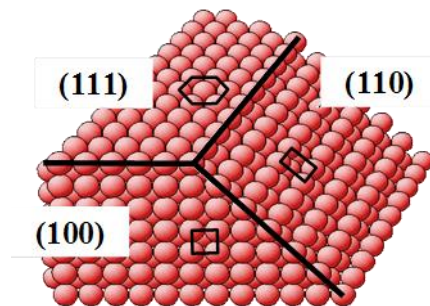


The shape of  $\gamma(\mathbf{n})$  changes from spherical, when the crystal is liquid (molten), to one with cusps at the positions of the most stable surfaces, which are the low Miller index planes. In these surfaces the atoms lose the least amount of bonds by the truncation of the crystal. For example, in an fcc or hcp crystal, the coordination goes from 12 in the bulk to 9 in the (111) surface, and to 8 in the (100) surfaces. The formation of singularities or cusps is due to the discrete nature of matter, so that when the orientation changes steps are formed. The interaction between steps determines the nature of the cusp. If  $E_s$  is the energy per unit step length, and if  $\theta$  is the angle away from the singular surface, the density of steps is  $1/a \cdot \sin(\theta)$ , where  $a$  is the step height. The extra surface energy per u. area ( $\gamma$ ) is then:

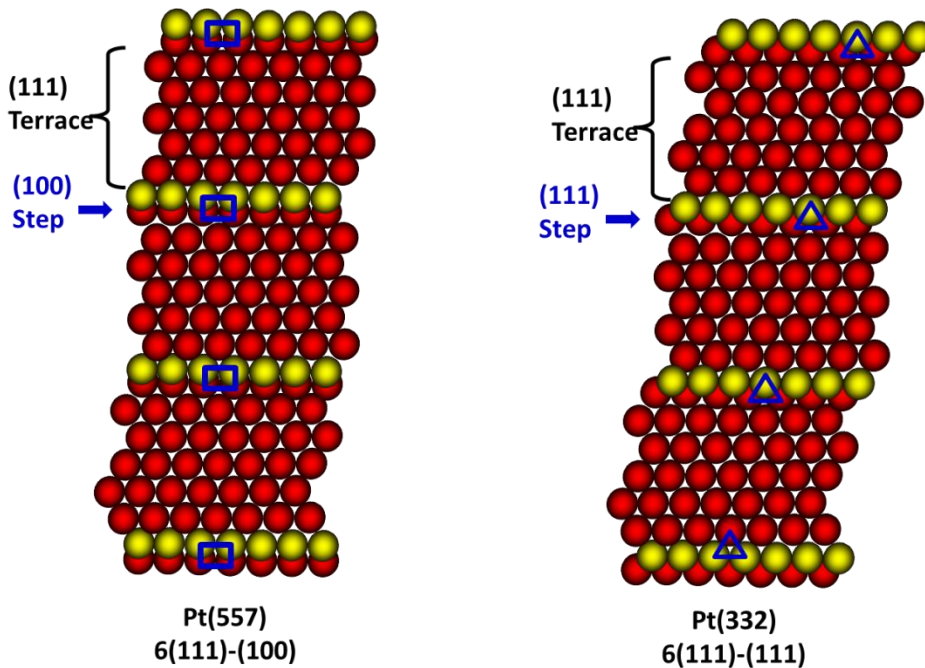
$$\gamma = E_s \cdot 1/a \cdot |\theta| \quad (\text{for small } \theta\text{'s}).$$

$$\text{So that: } \gamma(\theta) = \gamma(0) + E_s \cdot 1/a \cdot |\theta|$$

**low-index surfaces**



This represents a cone in a  $\gamma(\theta)$  plot. The cone needs not be symmetric because the value of  $E_s$  might be different for different azimuthal angles. Example:



This discussion assumed equidistant steps, separated by terraces on  $n$  atoms. One could imagine ‘pathological’ surfaces where terraces of different number of atoms,  $n$ ,  $n'$ , alternate. In this case the angle  $\theta$  could assume as many values as rational numbers .... Do such surfaces exist ? In other words: when cutting a crystal along a plane of a given orientation, what surface structure is produced? Unless we can “see” the atoms, all we know is the macroscopic angle.

The fact that experimentally stable stepped surfaces with periodically spaced steps exist implies that there is a repulsive interaction between steps, otherwise they will attract each other and collapse giving rise to faceting, discussed in next paragraph. The interaction is due to:

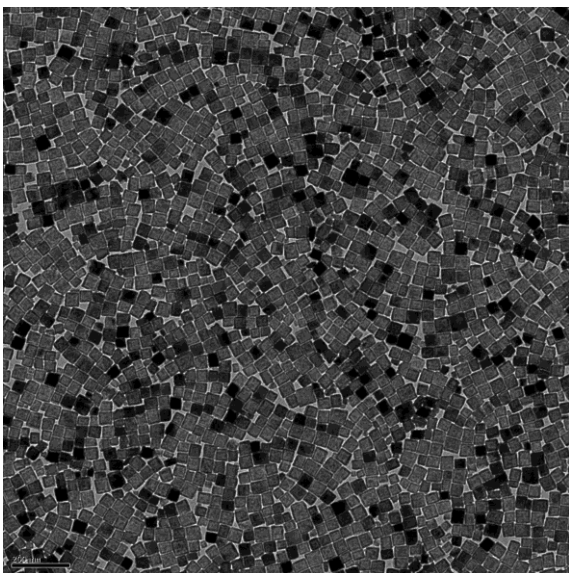
- a) Dipole electrostatic repulsion
- b) Elastic repulsion, all decaying as  $1/d^3$

## Kinetics

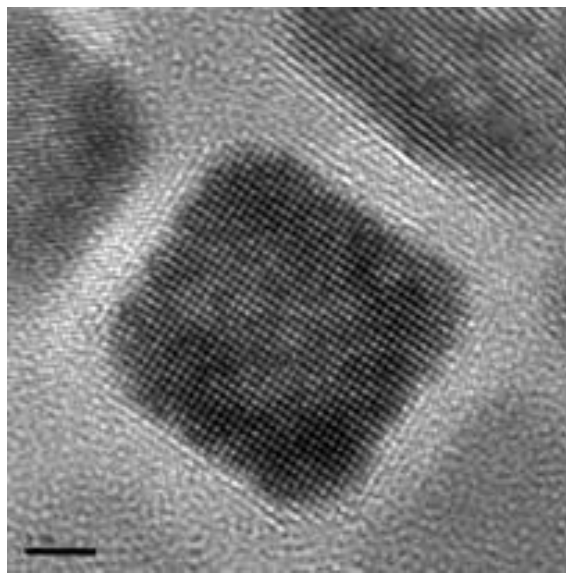
The equilibrium crystal shape rarely occurs because of kinetics.

Example: growth of nanoparticles with controlled shape by surfactant adsorption.

Pt nanocubes

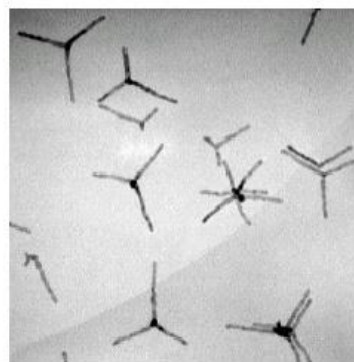
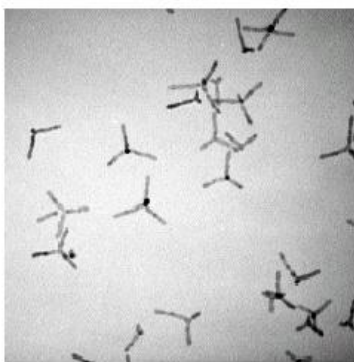


From Prof. Peidong Yang,  
Dept. Chemistry UCB

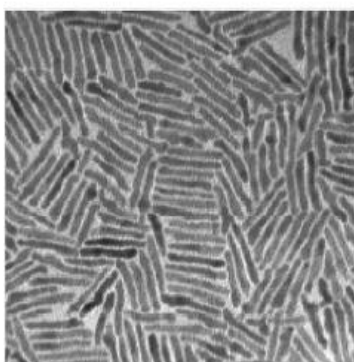
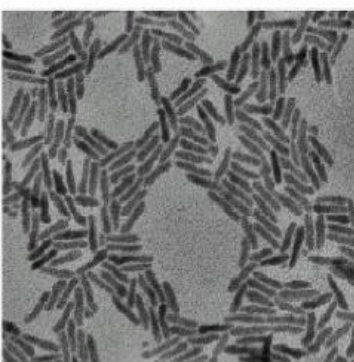
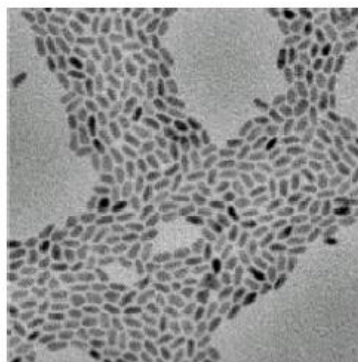


Tetrapods, Nanorods, ....

From Prof. Paul Alivisatos, Dept.  
Chemistry UCB



— 100 nm



— 50 nm